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Achievements and Future Development of the Physical Chemistry of Organic Raw Materials

When in 1946 I returned from the USA I found the Chemical Laboratories both at the Institute of Technology as well as at the Warsaw University completely destroyed. Since 1950 only was I able to start our scientific investigations. The three main problems which we could undertake to examine were:

1. The separation and purification of pyridine bases on a laboratory and industrial scale.

2. The elucidation of the process of ethanol dehydration by means of a mixture of benzene and a gasoline fraction, because it remained unexplained for 27 years since Guinot's patent claim.

3. The application of new cryometers allowing the use of the static method for examining of liquid-solid systems. One of these apparatuses is called differential, the other — dilatometric cryometer.

At that time my collaborators and myself had often the opportunity to visit the largest coal tar distillation plant "Hajduki", where conventional old methods of coal tar distillation and separation and purification of naphthalene and other constituents were used. It was then that the fundamental idea was developed, consisting in treating coal tars as polyazeotropic and polyeutectic systems. The term polyazeotropic mixture was formulated and extended to the majority of liquid organic raw materials. It was emphasized that in the course of distillation numerous azeotropes must

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be formed in any liquid raw material containing two, three or more series of homologues and their isomers. We have also assumed that the majority of fractions collected should be regarded as polyeutectic mixtures. In some particular cases solid solutions can also be found in different fractions collected.

It was obvious for us that the high and low temperature coal tars could form in the course of fractional distillation a very large number of known and unknown azeotropes containing two, three and even four constituents.

The following problems had to be solved:

1. investigation of new kinds of azeotropes including quaternary ones,

2. finding of an adequate type of ebulliometers for establishing with high accuracy the composition and normal boiling temperatures of the azeotropes under examination,

3. application of our knowledge on polyazeotropy and polyeutectic systems in order to considerably increase the yield of coal tar constituents. In the first place, naphthalene, pyridine and quinoline bases are the most important coal tar constituents, the yield of which should be increased to the highest level,

4. the pressing need of publishing not only in Polish but also in other languages two monographs: "Azeotropy and Polyazeotropy" and "Physical Chemistry of the Coal Tar" in order to secure the priority of Polish scientists in both subjects.

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It should be pointed out as regards point 4, that Russian (1958) and German (1959) editions of "Physical Chemistry of the Coal Tar" have already appeared, "Azeotropy and Polyazeotropy" has been translated into English language and arrangements was made to publish it in German language (in 1960 or 1961).

We received news that the American coal tar industry has put in operation some of our separation and purification methods. As regards 3- and 4-picoline, they are not separated now into pure components, but, according to our method, oxidised as a mixture of both. Owing to this no prices are quoted for these two bases individually on the market. On the contrary, the mixture of both these picolines is sold for the manufacture of isomeric nicotinic acid. This is a brief review of what we have been doing since 1953 in Poland.

It should be emphasized that the examination of azeotropes found in the coal tar has stimulated our scientists to examine a large number of azeotropes. Consequently, instead of four types of azeotropes listed in Lecat's and in Horsley's "Azeotropic Data", ten kinds are known up now. Among them are different kinds of quaternary as well as one quinternary azeotropes. In addition, a series of three liquid phase heteroazeotropes has been discovered.

In principle, instead of examining individual azeotropes as it has been done very often in the past, we are studying series of azeotropes formed by homologous series. Thus, many generalizations could be made offering material for thermodynamic calculation.

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Lately, the static cryometric method has been largely developed. We have been stimulated to do this by IUPAC's "Committee on Physico-Chemical Data and Standards" and by the National Bureau of Standards, USA. Both have undertaken the problem of comparing the efficiency and the accuracy of cryometric static and kinetic methods of purity tests. Extensive cryometric experiments are now under way in our laboratory for obtaining more accurate results than before.

Zięborak's initiative made it possible to examine many systems in which the transition from heteroazeotropes into homoazeotropes and zeotropes could be directly observed. The [redacted] data known in the past have been supplemented by numerous precise experiments conducted by Zięborak confirming all the predictions thus far formulated in several papers published by our group.

Malesiński has definitely developed his broad ideas concerning the theory of azeotropy as whole. A monograph on this subject will appear in 1960 or 1961.

The same author has published a series of papers dealing with what is called "ideal eutectics". Important conclusions resulted from Malesiński's theory. They have been described by Rylicki.

Interesting theoretical work has been done by Zięborak and his associates.

Stecki has developed the theory embracing the phenomena associated with binary and ternary heteroazeotropes.

It was obvious that some thermochemical measurements

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would be very useful for the development of thermodynamics of azeotropes. In view of this M. Wójcicka, A. Zielenkiewicz, M. Ciecierska-Tworek and E. Sadowska succeeded in collecting a number of important data in this field.

Independently, microcalorimetry and thermochemical investigations on sorbents-ionites have been successively carried out.

A close cooperation of our collaborators with two large coal tar plants has been established. The main problems consists in standarising the purity of coal tar constituents for pharmaceutical, dye, plastic, and other Polish industries as well as for export.

At present, it is difficult to predict the further lines of development of the physical chemistry of liquid organic raw materials. A more complete development of this new branch of science requires a great deal of research work. To do this, more than one group of scientists is needed. Much time is also necessary for developing the physical chemistry of the coal tar as such. What has been done thus far should be regarded as the first step in this direction. New methods and new apparatus should be used for building up the theoretical background and its practical applications. The first step has been made, we hope that further investigations will lead our knowledge to new important achievements.

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